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Reference: Japan patent No. H 6-348013 (JP, A), No. H 5-311097 (JP, A), No. S 57-49106 (JP, A), No. H 5-165029 (JP, A), No. H 8-50811 (JP, A)

Investigated field: (Int. Cl. DB name) G03 F 7/00 – 7/42, H 01 B 3/00, H 01 B 3/08

Detailed Report

(Name of invention)
photo-sensitive paste

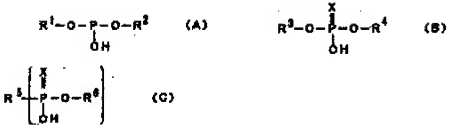
Sphere of the patent application

(Claim 1)
Claim 1 is concerning a photo-sensitive paste which has following characteristics. It is a photo-sensitive compound containing phosphorus, a photo-sensitive organic component, and inorganic particles. The phosphorus compound has a P-OH structure in the molecule.

(Claim 2)
Claim 2 is regarding the photo-sensitive paste in claim 1 which contains 0.01 to 10 wt. % of the phosphorus compound.

(Claim 3)
Claim 3 is regarding the photo-sensitive paste in claims 1 or 2 where the compound indicated by general formula (A) is the phosphorus containing compound.

Chemical formula



(R1 to R6: hydrogen carbide group with 1 to 10 carbon atoms and 0 to 4 oxygen atoms, X: oxygen atom or sulfur atom, m: integer from 1 to 4)

(Claim 4)
Claim 4 is regarding the photo-sensitive paste in claims 1 or 3 where glass particles make up 50 wt. % or more of the inorganic particles.

(Claim 5)
Claim 5 is regarding the photo-sensitive paste in claim 4 where the glass particles have a glass transition temperature (Tg) of 350 to 600°C.

(Claim 6)
Claim 6 is regarding the photo-sensitive paste in claims 4 or 5 where the glass particles contain 10 to 50 wt. % bismuth oxide or lead oxide.

(Claim 7)

Claim 7 is regarding the photo-sensitive paste in claims 4 to 6 where the glass particles contain 3 to 20 wt. % of an alkali metal oxide.

(Claim 8)

Claim 8 is regarding the photo-sensitive paste in claims 4 to 7 where the glass particles contain the following components (by oxide conversion).

SiO_2	5 to 50 wt. %
B_2O_3	5 to 50 wt. %
BaO	1 to 25 wt. %
Al_2O_3	1 to 10 wt. %

(Claim 9)

Claim 9 is regarding the photo-sensitive paste in claims 4 to 8 where the glass particles have an average particle diameter of 1 to 10 μm.

(Claim 10)

Claim 10 is regarding the photo-sensitive paste in claims 1 to 9 which contains 0.05 to 5 wt. % of a UV absorbing agent consisting of an organic dye.

(Claim 11)

Claim 11 is regarding the photo-sensitive paste in claims 1 to 10 which is used as a plasma display or plasma address liquid crystal display.

(Claim 12)

Claim 12 is regarding the photo-sensitive paste in claims 1 to 11 which is used for formation of the cell walls for a plasma display or plasma address liquid crystal display.

Detailed explanation of the invention

[0001]

(Field of industrial use)

This invention is concerning a new photo-sensitive paste. The photo-sensitive paste of this invention is used for pattern processing various displays such as a plasma display, plasma address liquid crystal display, or printed circuits.

[0002]

(Prior art)

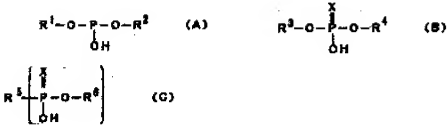
Recently, smaller printed circuits and displays with high definition are in demand. Because of this, improvements in the pattern processing technology are desired. Especially, materials which enable pattern processing with high aspect ratios and high accuracy are desired for forming green parting walls for a plasma display used for CPU of computers.

[0003] In the past, when pattern processing of inorganic material is performed, screen printing of a paste which consists of an inorganic powder in an organic binder has been used often. However, screen printing cannot be used to form a pattern with high accuracy.
[0004] To improve this problem, Japan patents No. H 1-296534, No. H 2-165538, and No. H 5-342992, disclose a method which uses photolithography using a photo-sensitive paste. However, since the sensitivity or resolution of the photo-sensitive paste is low, it is impossible to acquire parting walls with a high aspect ratio and high definition. For example, when a product with more than 80 μm thickness is pattern-processed, it requires multiple processes (screen printing, exposure, development), and it takes too long.
[0005] Japan patent No. H 2-165538 describes a method of forming parting walls by coating photo-sensitive paste on transcription paper and transcribing the transcription film onto a glass substrate. Japan patent No. H 3-57138 describes a method of forming parting walls by using a derivative paste to fill grooves in a photo-resist layer. Japan patent No. H 4-109536 describes a method of forming parting walls using a photo-sensitive organic film. However, since these methods require a transcription film, photo resist, or organic film, the number of processes is increased. In addition, parting walls with high definition or high aspect ratio have not yet been acquired.

[0006]
(Problem that this invention tries to solve)
The inventors of this invention conducted thorough research on photo-sensitive paste which can be used to form patterns with high aspect ratio and high definition. However, depending on the kind of organic particles used, the organic component may react to form a gel, and there are cases when the paste cannot be used because of viscosity.
[0007] The object of this invention is to acquire a stable photo-sensitive paste which controls gelling and can be used to form a pattern with high aspect ratio and high definition.

[0008]
(Steps for solution)
The object of this invention is to offer a photo-sensitive paste which has the following characteristics. It is a photo-sensitive compound containing phosphorus, a photo-sensitive organic component, and inorganic particles. The phosphorus compound has a P-OH structure in the molecule.

[0009]
(Embodiment of this invention)
In this invention, the "compound containing phosphorus" means a compound which contains 5 to 80 wt. % phosphorus in the molecule. By adding this phosphorus compound to the paste, a photo-sensitive paste with long pot life can be acquired. The compound containing phosphorus is effective if it contains a P-OH group in the molecule.
[0010] Compounds indicated by general formulae (A), (B), (C) are especially desirable.



(R1 to R6: hydrogen carbide group with 1 to 10 carbon atoms which also contains 0 to 4 oxygen atoms, X: oxygen atom or sulfur atom, m: integer number from 1 to 4)

Specific examples include the following compounds.
[0011] For instance, there are monoalkyl phosphite (C1 to 10) ester groups such as dibutyl phosphite, butyl phosphite, dimethyl phosphite, methyl phosphite, propyl phosphite, dipropyl phosphite, diphenyl phosphite, phenyl phosphite, isopropyl phosphite, diisopropyl phosphite, n-butyl-2-ethyl hexyl phosphite; dialkyl phosphite (C1 to 10) ester group, monoalkyl phosphate (C1 to 10) ester group such as dibutyl phosphate, butyl phosphate, dimethyl phosphate, methyl phosphate, propyl phosphate, dipropyl phosphate, diphenyl phosphate, phenyl phosphate, isopropyl phosphate, diisopropyl phosphate, n-butyl-2-ethyl hexyl phosphate; dialkyl phosphate (C1 to 10) ester group, aliphatic monocarbonate phosphate alkyl ester group, thiophosphoric acid compound which substitutes oxygen of ester phosphate in the above with sulfur, etc. Also, it is possible to use compounds with unsaturated groups such as acryl groups, methacryl groups, or vinyl groups for the alkyl part of the alkyl ester phosphite alkyl ester phosphate. Furthermore, it is possible to use a compound with a phosphoric acid group or phosphinic acid group.
[0012] The amount of these phosphoric compounds should be 0.01 to 10 wt. %, preferably 0.05 to 1 wt. %, to form a good paste with small influence on bonding with the substrate surface or photo-sensitivity.
[0013] A more preferred alkyl diphophate represented by hydroxy ethylylene diphophate is a compound with two or more phosphoric acid groups or phosphorous acid groups in the molecule.
[0014] The amount of these phosphorus compounds is 0.01 to 10 wt. %, preferably 0.05 to 1 wt. % in the paste. In this range, it is possible to acquire a good paste which has only a small influence on bonding with the substrate or photo-sensitivity.
[0015] They can be added by dissolving them in the paste, mixing with paste after dissolving in solvent, or surface treating the inorganic particles such as glass particles, etc. A specific method of surface treatment is a method in which the phosphorus compound is dissolved in a liquid such as organic solvent or water and then the solvent is removed.
[0016] Desirable solvents include methyl acetate, ethyl acetate, methanol, ethanol, etc. After removing the solvent, it is even better if heat treatment is administered for at least 12 hours at 50 to 200°C.
[0017] The photo-sensitive paste of this invention should contain at least 50 wt. % or more of inorganic particles which have been surface treated with phosphorus.

[0018] The inorganic particles in this invention are particles of glass or metal (gold, white gold, silver, copper, nickel, aluminum, palladium, tungsten, ruthenium oxide, etc.) that are generally used for electronics materials. Glass particles are especially effective in this invention. The glass particles should make up at least 50 wt. % of the inorganic particles.
[0019] Though the glass particles are not specifically restricted as long as they are conventional ones, glass which has the following composition is desired.

SiO_2	5 to 50 wt. %
B_2O_3	5 to 50 wt. %
BaO	1 to 25 wt. %
Al_2O_3	1 to 10 wt. %

[0020] The glass powder may also contain 2 to 20 wt. % TiO_2, ZrO_2, Y_2O_3, etc.
[0021] The glass powder should contain 3 to 60 wt. % SiO_2. If it is less than 3 wt. %, tightness, strength, and stability of the glass layer drops. A mismatch between the glass substrate and coefficient of thermal expansion occurs, and the CTE will not be in the desired range. If it is 60 wt. % or less, the thermal softening point becomes low and baking onto the glass substrate becomes possible.
[0022] By combining 3 to 60 wt. % B_2O_3, it is possible to improve the electrical, mechanical, and thermal properties of the material such as its electrical insulation value, strength, thermal coefficient of expansion, insulation layer tightness, etc. On the other hand, if it exceeds 60 wt. %, stability of the glass drops.
[0023] By adding BaO or Al_2O_3, a stable glass powder can be acquired.
[0024] ZnO should make up less than 30 wt. % of the material. If it exceeds 30 wt. %, the baking temperature is too low, and it cannot be controlled. Also, since resistivity becomes low, it is not desired.
[0025] The particle diameter of the glass powder is determined by the shape of the pattern to be made. 50 wt. % of the particles should have a diameter of 0.1 to 10 μm.
[0026] The inventors of this invention found that a pattern with a high aspect ratio can be formed using spherical glass particles.
[0027] The glass particles used in this case had a diameter of 1.0 to 7 μm (50 wt. %), 0.4 to 2 μm(10 wt. %), 4 to 10 μm (90 wt. %), and 0.2 to 3.0 m^2/g relative surface area. In addition, 50 wt. % or more of the glass particles should be 80% spherical as determined by the ratio of spherical particles (includes oval or egg shapes) after observing the particles using an electronic microscope.
[0028] The glass transition temperature (Tg) of the glass particles used to form a pattern on a glass substrate should be 350 to 600°C. Glass powder with this thermal characteristic can be acquired by introducing lead oxide, bismuth oxide, and an alkali metal oxide. This invention is especially effective if the glass particles contain these materials.
[0029] Adding 10 to 50 wt. % Bi_2O_3 and PbO makes it easier to control the thermal characteristics.
[0030] Furthermore, it is possible to add metal oxides such as Na_2O, Li_2O, K_2O, etc. However, these materials should be kept to less than 20 wt. % to promote water-

resistance. However, adding 3 to 15 wt. % of these alkali metal oxides helps control the softening temperature, refractive index, and coefficient of thermal expansion.

[0031] Adding 5 to 25 wt. % of Bi_2O_3 and amount and 3 to 10 wt. % alkali metal oxide makes it possible to acquire a glass with an excellent softening temperature, refractive index, coefficient of thermal expansion, and electrical stability. In the past, such glass has not been used for photo-sensitive paste because of gelling. However, this invention makes its use possible.

[0032] A glass powder with 1.50 to 1.65 refractive index for the g line (436 nm) of mercury makes it possible to adjust the refractive index of the organic component. A pattern with high accuracy can be produced by controlling diffraction.

[0033] "Photo-sensitive organic component" used in this invention means an organic component which contains a photo-sensitive compound in the paste (part which excludes the inorganic part).

[0034] The photo-sensitive organic component may contain one of the following reactive components: photo-sensitive monomer, photo-sensitive oligomer, photo-sensitive polymer, and additives such as a binder, photo polymerization initiator, UV absorbing agent, sensitizer, sensitizing assistance agent, polymerization prohibiting agent, plasticizer, viscosity agent, organic solvent, oxidation preventing agent, dispersing agent, or an organic or inorganic precipitation preventing agent.

[0035] The photo-sensitive paste used in this invention should contain at least 10 wt. % or more of the reactive component in the photo-sensitive organic component to promote sensitivity to light. It is even better if it is 30 wt. % or more.

[0036] The reactive component can be photo-insoluble or photo-soluble. Photo-insoluble types include:

(1) ones which contain functional monomers, oligomers, or polymers with at least one unsaturated group in the molecule;
(2) ones which contain photo-sensitive compounds such as aromatic diazo compounds, aromatic azido compounds, organic halogen compounds, etc.;
(3) ones which are called diazo resin such as condensation of diazo based amine and formaldehyde.

Photo-soluble types include:

(4) ones with a complex with inorganic salt or organic acid of diazo compound, quinone diazo group;
(5) ones which bond a quinone diazo group with an appropriate polymer binder such as naphthoquinone 1,2-diazido-5-ester sulfonate of novolac resin, phenol.

[0037] All of these can be used for the reactive component in this invention. However, (1) is the most convenient photo-sensitive paste.

[0038] The reactive monomer used in this case is a compound with a carbon-carbon unsaturated bond. Specific examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, sec-butyl acrylate, iso-butyl acrylate, tert-butyl acrylate, n-pentyl acrylate, allyl acrylate, benzyl acrylate, butoxy ethyl acrylate, butoxy triethylene glycol acrylate, cyclo hexyl acrylate, dicyclo pentanyl acrylate, dicyclo pentenyl acrylate, 2-ethyl hexyl acrylate, glycerol acrylate, glycidyl acrylate, heptadeca fluoro decyl acrylate, 2-hydroxy ethyl acrylate, isobonyl acrylate, 2-hydroxy propyl acrylate, isodexyl acrylate, oso octyl acrylate, lauryl acrylate, 2-methoxy ethyl acrylate, methoxy ethylene glycol acrylate, methoxy diethylene glycol acrylate,

octafluoro pentyl acrylate, phenoxy ethyl acrylate, stearyl acrylate, trifluoro ethyl acrylate, allylized cyclo hexyl diacrylate, 1,4-butane diol diacrylate, 1,3-butyrene glycol diacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, polyethylene glycol diacrylate, dipenta erythritol hexa acrylate, dipenta erythritol monohydroxy penta acrylate, ditrimethylol propane tetra acrylate, glycerol diacrylate, methoxidized cyclo hexyl diacrylate, neopentyl glycol diacrylate, propylene glycol diacrylate, polypropylene glycol diacrylate, triglycerol diacrylate, trimethylol propane triacrylate, acryl amide, amino ethyl acrylate, and one which has changed part of all of acrylate in molecule of the compound in the above, γ-methacryloxy propyl trimethoxy silane, 1-vinyl-2-pyrrolidone, etc.

[0039] In this invention, one or more of these can be used. In addition to these, by adding unsaturated carbonic acid, it is possible to improve developing after photo-sensitizing. Specific examples of unsaturated carbonic acid include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, or anhydrides of these.

[0040] The photo-sensitive oligomer or polymer can be the reaction monomer above, a methacrylate monomer or acrylate monomer which has an aromatic ring such as a benzene ring or naphthalene ring; for example, phenyl (meth)acrylate, phenoxy ethyl (meth)acrylate, benzyl (meth)acrylate, 1-naphthyl (meth)acrylate, 2-naphthyl (meth)acrylate, bisphenol A di(meth)acrylate, di(meth)acrylate of bisphenol A-ethylene oxide addition substance, thiophenol (meth)acrylate, benzyl mercaptane (meth)acrylate, monomers which replace 1 to 5 hydrogen atoms in these aromatic rings with chlorine or bromine atoms, or oligomers or polymers acquired by polymerizing at least one of the following: styrene, p-methyl styrene, o-methyl styrene, m-methyl styrene, chlorinated styrene, brominated styrene, α-methyl styrene, chlorinated α-methyl styrene, brominated α-methyl styrene, chloro methyl styrene, hydroxy methyl styrene.

[0041] Polymerization can be done with another reactive monomer so that the ratio of these monomers will be 10 wt. % or more, preferably 35 wt. % or more. The monomer to be copolymerized can be a compound with the above carbon-carbon unsaturated bond.

[0042] Also, by copolymerizing with unsaturated carbonic acid, it is possible to improve developing after photo-sensitizing. Specific examples of unsaturated carbonic acid include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl acetate, or anhydrides of these. This invention is especially effective when a polymer which has a carboxyl group in the organic component is used.

[0043] The acid value (AV) of the polymer or oligomer which has a carboxyl group in the side chain acquired above should be 50 to 180, preferably 70 to 140. If the acid value is less than 50 or more than 180, the developable range becomes narrow, and a pattern with high definition is hard to acquire.

[0044] By adding a photo-reactive group to the side chain or end of the molecule of the polymer or oligomer above, the material can be made photo-sensitive. A desirable photo-reactive group has an ethylene type unsaturated group. Examples include vinyl groups, allyl groups, acryl groups, methacryl groups, etc.

[0045] Methods of adding a side chain to the oligomer or polymer above include a method which adds and reacts an ethylene type unsaturated compound which has glycidyl group or isocyanate group, chloride acrylate, chloride methacrylate, or allyl

chloride with a mercapto group, amino group, hydroxyl group, or carboxyl group in the polymer.

[0046] Suitable ethylene type unsaturated compounds with a glycidyl group include glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, ethyl acrylate glycidyl, crotonyl glycidyl ether, glycidyl ether crotonate, glycidyl ether isocrotonate, etc.

[0047] Suitable ethylene type unsaturated compounds with an isocyanate group include (meth)acryloyl isocyanate, (meth)acryloyl ethyl isocyanate, etc. The ethylene type unsaturated compound which has a glycidyl group or isocyanate group or chloride acrylate, chloride methacrylate, or allyl chloride should make up 0.05 to 1 mol per weight of the mercapto group, amino group, hydroxyl group, or carboxyl group in the polymer.

[0048] It is possible to add components such as binders, photo polymerization initiators, UV absorbing agents, sensitizers, sensitizing assistance agents, polymerization prohibiting agents, plasticizers, viscosity agents, organic solvent, oxidation preventing agents, dispersing agents, or organic or inorganic precipitation preventing agents to the photo-sensitive paste used in this invention.

[0049] Suitable binders include polyvinyl alcohol, polyvinyl butyral, ester methacrylate polymer, ester acrylate polymer, ester-acrylate ester methacrylate copolymer, α-methyl styrene polymer, butyl methacrylate resin, etc.

[0050] Specific examples of photo-polymerization initiators include benzophenone, o-benzoyl methyl benzoate, 4,4-bis (dimethyl amine) benzophenone, 4,4-bis (diethyl amino)benzo phenone, 4,4-dichloro benzo phenone, 4-benzoyl-4-methyl diphenyl ketone, dibenzyl ketone, fluolenone, 2,2-diethoxy acetophenone, 2,2-dimethoxy-2-phenyl-2-phenyl acetophenone, 2-hydroxy-2-methyl propiophenone, p-t-butyl dichloro acetophenone, thioxantone, 2-methyl- thioxantone, 2-chloro thioxantone, 2-isopropyl thioxantone, diethyl thioxantone, benzyl, benzyl dimethyl ketanol, benzyl-2-methoxy ethyl acetal, benzoin, benzoin methyl ether, benzoin butyl ether, anthraquinone, 2-t-bityl anthraquinone, 2-amyl anthraquinone, β-chlor anthraquinone, anthrone, benzanthrone, dibenzo suberone, methylene anthrone, 4-azido benzal acetophenone, 2,6-bis (p-azido benzylidene) cyclohexanone, 2,6-bis (p-azido benzylidene)-4-methyl cyclohexanone, 2-phenyl-1,2-butadion—2-(o-methoxy carbonyl)oxim, 1-phenyl-propane dion-2-(o-ethoxy carbonyl)oxim, 1,3-diphenyl-propane trion-2-(o-ethoxy carbonyl)oxim, 1-phenyl-2-3-ethoxy-propane trion-2-(o-benzoyl)oxim, Mihler's ketone, 2-methyl-4-[4-(methyl thio)phenyl]-2-morpholino-1-propanone, naphthalene sulfonyl chloride, quinoline sulfonyl chloride, N-phenyl thioacrylidone, 4,4-azobis isobutylonitrile, diphenyl disulfide, benzthiazole disulfide, triphenyl phosphine, camphorquinone, carbon tetrabromide, tribromo phenyl sulfone, benzoin peroxide, and combinations of photo-reduction type color elements such as eosin, methylene blue and reducing agents such as ascorbic acid, triethanol amine, etc. In this invention, one or more of these can be used. The amount of photo polymerization initiator should be in the range of 0.05 to 10 wt. %, preferably 0.1 to 5 wt. % per reaction component. If the amount of polymerization initiator is too small, photo sensitivity is inferior. On the other hand, if it is too much, the amount of exposed part remaining may become too small.

[0051] It is effective to add UV absorbing agents which consist of organic dye. By adding a photo-absorbing agent with a high UV absorbing effect, high aspect ratio, high definition, and high detail can be acquired. The UV absorbing agent commonly consists of organic dye. Among these, organic dyes which have a high UV absorbance coefficient

at 350 to 450 nm is suitable. Specifically, azo based dye, amino ketone based dye, xanthine based dye, quinoline based dye, amino ketone based dye, anthraquinone based, benzophenone based, diphenyl cyano acrylate based, triazine based, or p-amino benzoate based dye can be used. Organic dye is good since it does not remain in the insulating film after sintering and can reduce loss of insulation properties when it is used as the photo-absorbing agent. Among these, azo based and benzophenone based dyes are good. The amount of organic dye is 0.05 to 5 wt. parts. If it is less than 0.05 wt. %, the effect of adding UV photo-absorbing agent is reduced. On the other hand, if it exceeds 5 wt. %, insulation characteristics after sintering drop, which is not preferred. More preferably, it is 0.15 to 1 wt. %. One example of a method of adding UV photo-absorbing agent which consists of organic pigment follows. First, a solution of organic pigment dissolved in organic solvent is manufactured beforehand. Next, glass powder is mixed in the organic solvent and dried. According to this method, a capsule type powder with organic film on the surface of individual glass powder can be manufactured.

[0052] A sensitizer is used for increasing sensitivity. Specific examples of sensitizers include 2,4-diethyl thioxantone, isopropyl thioxantone, 2,3-bis (4-diethyl amino benzal)cyclo pentanone, 2,6-b9s)4-dimethyl aminibenzal)cyclohexanone, 2,6-bis(4-dimethyl aminobenzal)4-methyl cyclohexanone, Mihler' ketone, 4,4-bis (diethyl amino)-benzophenone, 4,4-bis (dimethyl amino)-chalcone, 4,4-bis (diethyl amino) chalcone, p-dimethyl amino cinnamylidene indanone, p-dimethyl amino benzylidene indanone, 2-(p-dimethyl amino phenyl vinylene)-isonaphtha thiazole, 1,3-bis (4-dimethyl aminobenzal)acetone, 1,3-carbonyl-bis (4-diethyl aminobenzal)acetone, 3,3-carbonyl-bis (7-diethyl amino coumarin), N-phenyl-N-ethyl ethanol amine, N-phenyl ethanol amine, N-tolyl diethanole amine, N-phenyl ethanol amine, dimethyl amino benzoate isoamyl, diethyl amino benzoate isoamyl, 3-phenyl-5-benzoyl thio-tetrazole, 1-phenyl-5-ethoxy carbonyl thio-tetrazole, etc. In this invention, they can be used either alone or in combinations of two or more kinds. The sensitizer may contain precuts that can also be used as photo-polymerization initiators. When a sensitizer is added to the photo-sensitive paste of this invention, it is normally 0.05 to 5 wt. %, preferably 0.1 to 2 wt. % per reactive component. If the amount of sensitizer is too small, it does not improve photo-sensitivity. On the other hand, if the amount is too much, the amount of exposed portion remaining may become small.

[0053] A polymerization prohibiting agent is added in order to improve thermal stability during storage. Specific examples of polymerization prohibiting agents include hydroquinone, mono esterified substance of hydroquinone, N-nitroso diphenyl amine, phonothiazine, p-t-butyl catechol, N-phenyl naphthyl amine, 2,6-di-t-butyl-p-methyl phenol, chloranil, pyrogallol, etc. The amount of polymerization prohibiting agent is normally 0.001 to 1 wt. % of the photo-sensitive paste.

[0054] Specific examples of plasticizers include dibutyl phthalate, dioctyl phthalate, polyethylene glycol, glycerin, etc.

[0055] Anti-oxidant is added in order to prevent oxidation of the acryl based copolymer during storage. Specific examples of antioxidants include 2,6-di-t-butyl-p-cresol, butylized hydroxy anisole, 2,6-di-t-4-ethyl phenol, 2,2-methylene-bis-(4-methyl-6-t-butyl phenol), 2,2-methylene-bis-(4-ethyl-6-t-butyl phenol), 4,4-bis-(3-methyl-6-t-butyl phenol), 1,1,3-tris-(2-methyl-6-t-butyl phenol), 1,1,3-tris-(2-methyl-4-hydroxy-t-butyl phenyl)butane, bis [3,3-bis-(4-hydroxy-3-t-butyl phenyl)butyric acid] glycol ester,

dilauryl thio dipropionate, triphenyl phosphite, etc. The amount of antioxidant is normally 0.001 to 1 wt. % of the paste.

[0056] If viscosity needs to be adjusted, it is possible to add organic solvent to the photo-sensitive paste of this invention. This organic solvent may be , for example, methyl cellosolve, ethyl cellosolve, butyl cellosolve, methyl ethyl ketone, dioxane, acetone, cyclo hexanone, cyclo pentanone, isobutyl alcohol, isopropyl alcohol, tetra hydro furan, dimethyl sulfoxide, γ-butylolactone, bromo benzene, chloro benzene, dibromo benzene, dichloro benzene, bromo benzoate, chloro benzoate, or mixtures of organic solvent which contains one or more of these.

[0057] When paste is manufactured, metal oxides of glass particles react with the organic component and it becomes tacky. In order to prevent this, a gel preventing agent can be used.

[0058] The photo-sensitive paste is normally manufactured by preparing various components of inorganic particles, UV absorbing agents, photo-sensitive polymer, photo-sensitive monomer, photo-polymerization initiator, glass flit, and solvent, etc., according to a predetermined composition and then mixing and dispersing it uniformly with three-rollers or a kneader. The viscosity of the paste is adjusted appropriately depending on the ratio of inorganic particles, viscosity agent, organic solvent, plasticizer, and precipitation preventing agent. The desired range is 200 to 200,000 cps.

[0059] Next, one example in which a pattern process is administered using photo-sensitive paste is going to be explained. However, this invention is not limited to this example only.

[0060] Part or all of the surface of a glass or ceramic substrate is covered with photo-sensitive paste by a conventional method such as screen printing, bar coating, roll coating, etc. The thickness of the coating can be adjusted by selecting the number of applications, screen mesh, or viscosity of the paste.

[0061] When the paste is spread on the glass substrate, the substrate can be surface treated in order to increase bonding between the substrate and coating. The surface can be treated using a solution of a silane coupling agent such as vinyl trichloro silane, vinyl trimethoxy silane, vinyl trimethoxy silane, tris-(2-methoxy ethoxy)vinyl silane, γ-glycidexy propyl trimethoxy silane, γ-(methacryloxy propyl) trimethoxy silane, γ (2-amino ethyl) amino propyl trimethoxy silane, γ-chloro propyl trimethoxy silane, γ-mercapto propyl trimethoxy silane, γ-amino propyl trimethoxy silane, or an organic solvent such as organic titanium, organic aluminum, organic zirconium, etc. A 0.1 to 5 % solution of silane coupling agent or organic metal in an organic solvent such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, methyl alcohol, ethyl alcohol, propyl alcohol, or butyl alcohol is used. Next, after this surface treatment solution is uniformly applied on the substrate by spin coating , etc., it is dried for 10 to 60 minutes at 80 to 140°C, and the surface treatment is complete.

[0062] This coating is exposed to light using a photo mask. The type of mask depends on the kind of photo-sensitive organic component, either negative type or positive type. The active rays in this case can be, for example, near UV, UV, electron beam, X rays, etc. Among these, UV is preferred. The light source may be, for example, a low pressure mercury lamp, high pressure mercury lamp, ultra high pressure mercury lamp, halogen lamp, sterilizing lamp, etc. Among these, a super high pressure mercury lamp is suitable. Although exposing conditions differ depending on the coating thickness,

exposure is performed for 1 to 30 minutes using a super high pressure mercury lamp with 5 to 100 mW/cm^2 output.

[0063] After applying the photo-sensitive paste, an oxygen shielding film is arranged on its surface to improve the pattern shape. PVA is one example of an oxygen shielding film which is formed as follows. A Solution with 0.5 to 5 wt. % concentration is uniformly applied to the substrate by a method such as spin coating, and it is dried for 10 to 60 minutes at 70 to 90°C. The preferred concentration of the PVA solution is 1 to 3 wt. %. If it is in this range, sensitivity is improved even more. The following reasons are estimated as to why sensitivity is improved by PVA application. When the reactive component is photo-reacted, if oxygen is present, it is thought to interfere with the sensitivity of photo-curing. However, since the PVA shields excess oxygen, sensitivity to light is improved, which is good. In addition to PVA, a water-soluble transparent polymer, for example, cellulose based methyl cellulose can also be used.

[0064] After exposing to light, development is done using a developing solution. In this case, it is done by immersion or spraying. The developing solution is an organic solvent that can dissolve the organic component of the photo-sensitive paste. It is also possible to add water in the range where it does not harm the dissolving power of the organic solvent. When a compound with a carboxyl group exists in the photo-sensitive paste, development can be done using an alkali solution such as sodium hydroxide or calcium hydroxide. However, an organic alkali solution is preferred since the alkali component is easier to remove during sintering. The organic alkali can be a conventional amine compound. For example, there are tetra methyl ammonium hydroxide, trimethyl benzyl ammonium hydroxide, monoethanol amine, diethanol amine, etc. The concentration of the alkali solution is normally 0.01 to 10 wt. %, preferably 0.1 to 5 wt. %. If the alkali concentration is too low, the unexposed portion is not removed. On the other hand, if the alkali concentration is too high, it peels off part of the pattern and the exposed part may have corrosion, which is not desired.

[0065] Next, sintering is done in a sintering oven. Although the sintering atmosphere or temperature depends on the kind of paste or substrate, it is normally sintered in a gas or nitrogen atmosphere at 400 to 1000°C. When pattern processing is done on a glass substrate or silver is used as the inorganic particles, it is kept for 10 to 60 minutes at 520 to 610°C temperature, and then sintering is performed.

[0066] In the above process, the part can be heated to 50 to 300°C for drying or pre-reaction.

[0067]

Example of practice

In the following, this invention is going to be explained specifically using one example of practice. However, this invention is not restricted to only this example. Concentration (%) in the example of practice and example of comparison is weight %.

[0068] In the example of practice, a photo-sensitive paste which consists of glass particles and a photo-sensitive organic component was manufactured in the following order. First, each component of the photo-sensitive organic component is dissolved while heated to 80°C. After that, inorganic particles are added, and they are kneaded by a kneader, and the paste was finished.

[0069] Next, a 30 cm square soda glass substrate was coated to a thickness of 130 μm using a doctor blade, and it was dried for 30 minutes at 80°C. However, depending on paste, some products gelled and could not be coated. This situation was evaluated after 1 day, 3 days, and 7 days. The products that were applied were exposed and developed by the following methods.

[0070] Next, the material was exposed using a striped mask for parting walls for a plasma display. This mask was chromium that formed a striped pattern with 220 μm pitch and 60 μm line width. It was exposed using UV from a super high pressure mercury lamp at 50 mW/cm^2 output.

[0071] After that, it was immersed in a 1 % solution of monoethanol amine, and development was done. In addition, the glass substrate was dried for 1 hour at 120°C, and sintering was done for 15 minutes at 560°C.

[0072] The pattern (line width 50 μm X height 100 μm, pitch 220 μm is target) was evaluated by observation with an electronic microscope.

[0073] The composition of the photo-sensitive paste in this example of practice is indicated in the following.

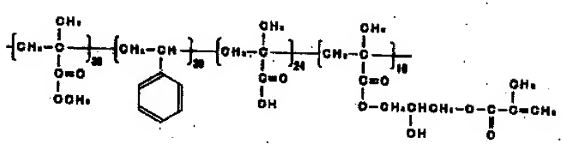
Glass particles: see below	80.0 wt. parts
Photo-sensitive monomer: TMPTA	9.0 wt. parts
Photo-sensitive polymer: polymer 1	13.3 wt. parts
Photo polymerization initiator: MTPMP	2.0 wt. parts
UV absorbing agent: sudan	0.1 wt. part
Sensitizer: DET	2.0 wt. parts
Sensitizing assisting agent: EPA	1.0 wt. part
Organic solvent: γ-BL	21.7 wt. parts

[0074] Concerning the abbreviations, see the note below.

[0075] (numbers in the polymer structure indicate the mol ratio of each monomer)

TMPTA: trimethylol propane triacrylate polymer 1:

Chemical formula



MTPMP: 2-methyl-1-[4-(methylthio)phenyl]-2-morphorino propane-1

Sudan: azo base dye, $C_{24}H_{20}N_4O$

DET: 2,4-diethyl thioxantone

EPA: p-dimethyl amino benzoate ethyl ester

γ-BL: γ-butylolactone

Concerning gel prevention agent, in examples of practice 1 to 8, after it was dissolved in isopropyl alcohol, it was removed under reduced pressure at 50°C. After that, heating was done for 5 hours at 80°C, and gel prevention agent was applied to the inorganic particles. In example of practice 9, it was not applied to the surface, but it was dissolved in the paste.

[0076] In the examples of practice, in examples of practice 1 to 5 and example of comparison 1, glass 1 was used. In examples of practice 6 to 9 and example of comparison 2, glass 2 was used.

[0077]

glass 1

Bi_2O_3: 37 wt. %

B_2O_3: 14 wt. %

SiO_2: 17 wt. %

ZnO: 16 wt. %

BaO: 8 wt. %

Al_2O_3 14 wt. %

Na_2O: 4 wt. %

Spherical rate: 85 %, refractive index 1.73, 50 wt. 5 average particle diameter: 3.2 μm

glass 2

Bi_2O_3: 37 wt. %

B_2O_3: 14 wt. %

SiO_2: 17 wt. %

ZnO: 16 wt. %

BaO: 8 wt. %

Al_2O_3 14 wt. %

Na_2O: 4 wt. %

Spherical rate: 88 %, refractive index 1.58, 50 wt. 5 average particle diameter: 3.3 μm

Table 1

	Gelling prevention agent	Used amount	After 3 days	After 7 days	After 14 days
Ex. of practice 1	DBPO	0.5 %	O	O	Δ
Ex. of practice 2	DBP	0.2 %	O	Δ	X
Ex. of practice 3	DBP	0.5 %	O	O	O
Ex. of practice 4	HEDP	0.1 %	O	O	O
Ex. of practice 5	HEDP	0.2 %	O	O	O
Ex. of practice 6	HEDP	0.01 %	O	Δ	Δ

Ex. of practice 7	HEDP	0.1 %	O	O	O
Ex. of practice 8	HEDP	0.5 %	O	O	O
Ex. of practice 9	MEP	3.5 %	O	O	Δ
Ex. of comparison 1	Not used		X	X	O
Ex. of comparison 2	Not used		X	X	X

O: a good pattern was acquired from the paste.
Δ: Although application was possible, development was inferior, and a good pattern could not be acquired.
X: Application of paste was impossible.

DBPO: dibutyl phosphate
DBP: dibutyl phosphite
HEDP: hydroxy ethylylene diphosphate
MEP: methacryloyl ethyl ester phosphate

[0078]
(Effects of this invention)

According to the gel prevention agent of this invention, it is possible to use a photo-sensitive paste that enables pattern processing with high aspect ratio and high accuracy using a stable process. This can be used to form, displays, thick films for circuit boards, and highly accurate pattern processing. Precision is improved and the process is simplified.

[0079] Especially, it is possible to form parting walls for a plasma display with high definition easily.